

NATURAL AND ANTHROPOGENIC FEATURES INFLUENCING WATER QUALITY IN NE BUENOS AIRES, ARGENTINA

G. Galindo¹, C. Sainato², C. Dapeña³, J.L. Fernández-Turiel⁴, D. Gimeno⁵, M.C. Pomposiello⁶, and H. Panarello⁷

¹ Fac. de Cs. Ex y Nat. UBA-CONICET, Argentina. ggalindo@mail.retina.ar

² Fac. de Agronomía, UBA, Argentina. csainato@mail.agro.uba.ar

³ Fac. de Cs. Ex y Nat. UBA-CONICET, Argentina. dapenna@ingeis.uba.ar

⁴ Instituto J. Almera, CSIC, Barcelona, España. jlfernandez@ija.csic.es

⁵ Fac. Geología, Univ. Barcelona, Barcelona, España. domingo@natura.geo.ub.es

⁶ CONICET, Argentina. cpompo@ingeis.uba.ar

⁷ CONICET, Argentina. hector@ingeis.uba.ar

Abstract

This work study the water quality of the Pergamino River watershed in the Undulated Pampa in the northeast of the Argentinean Province of Buenos Aires. Temperature, pH, specific conductivity, Na, K, Mg, Ca, SO₄²⁻, Cl⁻, HCO₃⁻, NO₃⁻, Si, Ag, Al, As, B, Ba, Be, Br, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, P, Pb, Se, Tl, U, V, Zn, and the δ¹⁸O y δ²H isotope ratios were monitored in eighteen sampling stations. Groundwater and surface water are of sodium bicarbonate type, evolving to sodium sulfate-chloride type in the case of surface water. Natural processes related to the seasonal alternation of humid and dry periods (precipitation and evapotranspiration), and the ion exchange processes during water-rock interaction are the main factors influencing water quality, especially in relation with the water salinity. Point pollution sources (septic wells and other domestic effluents) induce the increase of nitrate concentration. On the other hand, pH, NO₃⁻, Al, As, B, Fe, and Mn exceed the respective Argentinean reference thresholds in different sampling stations for human drinking water, B, Mo, U, and V for irrigation, and V and Zn for cattle drinking water.

Key Words: water - quality - Buenos Aires

INTRODUCTION

Water resources are a key factor for the planning of the sustainable regional development of agriculture and cattle farming in the Pergamino River watershed, which is located in the waterhead of Arrecifes River in the Undulated Pampa in the northeast of the Argentinean Province of Buenos Aires. The watershed of the Pergamino River is an important area for agriculture production (wheat and sunflower), and in a less scale for bovine cattle. The proximity to the consumption areas and a favorable price setting during the last decade produced an increase of these activities and consequently an increase of the water demand. The low slope of the terrain, its geological features, and the dry and humid alternating climatic periods, favor flooding events and reduce the cultivation yields, limiting seriously the extensive introduction of irrigation outcrops.

The 30% of wells from the Pergamino River watershed has risk of salinization and the 40% has risk of sodification (Losinno et al., 2002). Both risks are predominant in the NW of the study area. The salinity increases at the flooding plains of the rivers and towards their beds (discharge zones) with

values of specific conductivity greater than 1000 μS/cm at the north and south of Pergamino city.

The aim of this work is to elucidate the natural and anthropogenic features influencing water quality in the Pergamino River watershed in order to contribute to the regional sustainable development of the agriculture and livestock.

Study area

The study area is located in the Rosario basin at the NE of Buenos Aires Province, Argentina (Figure 1). The Pergamino River flows through this flat area (between 80 and 50 m a.s.l.), which is a part of the Undulated Pampa region. It is a tributary of the Arrecifes River, a tributary of the Parana River. The climate is characterized by the cyclic fluctuation of dry and humid periods. The annual average temperature is 16 °C and the annual average precipitation is 970 mm. The maximum precipitation occurs in summer (January). The precipitation is enough to obtain a positive water balance (Sainato et al., 1997).

The geology of the area has been investigated for hydrogeologically purposes by means of vertical electrical soundings (Sainato et al., 2001, 2002). Two main horizontal sedimentary

sequences occurs in the area, the Plio-Pleistocene Puelches sequence in the lower part and the Middle-Upper Quaternary Pampeana sequence in the upper levels. The Puelches sequence consists of loess, silt-clays and sands of the local typical tosca (calcium carbonate precipitate). The Pampeana sequence thickness varies between 20 and 120 m (Santa Cruz and Silva Busso, 1995). This sequence is constituted by loess, silt-clay layers alternating with sandy layers and more or less continuous levels of calcium carbonate (tosca) made up of rounded agglomerates. Argiudoll type soils predominates over the Pampeana sequence, although locally exist also natraquoll soils. They have a moderate to high cation exchange capacity, with calcium as governing cation for argiudolls and sodium as dominant exchanged cation in natraquolls. Both soils are loamy and nutrient-rich, with good aptitude for agriculture.

Groundwater exploitation is centered in the Pampeano aquifer, although some wells for irrigation obtain the water also from the Puelches aquifer. The groundwater for domestic and farming uses is mainly obtained from the upper part of the Pampeano aquifer. This upper part of the Pampeano aquifer shows unconfined characteristics, while is a semiconfined multilayer aquifer in the lower part.

In general, the direction of the regional phreatic runoff is from WNW to ESE at the northern part of Buenos Aires Province. There is a direct recharge related to the precipitation, and an indirect recharge by upward flow (Santa Cruz and Silva Busso, 1995).

The Pampeano aquifer shows a decrease of the water salinity in the same direction that the regional phreatic runoff, being the dry residue of 1000 mg l⁻¹ at Pergamino and 800 mg l⁻¹ at Arrecifes (approximately at 50 km to the SE of the study zone). Models obtained from vertical electrical soundings showed a fresh-salty water interface, which deepens towards the SE along the Pergamino River, also having a greater depth at the left margin (Sainato et al., 2001, 2002). Results were compared with conductivity of water samples and well data. It was concluded that there is a deterioration of water quality below 50 m depth at Pergamino zone and below 100 m near Arrecifes.

SAMPLING AND METHODS

Eighteen sampling stations were defined in the Pergamino River watershed, ten for groundwater and eight for surface water monitoring (Figure 1). Its location was determined by GPS. The groundwater sampling depth was between 25 and 70

m. These wells are representative of those used for disperse population supply (drinking water and farming uses). Surface water sampling stations are representative of the water quality evolution through the watershed.

Temperature, pH, and specific conductivity were determined in situ. The concentrations of HCO₃⁻ and NO₃⁻ were determined with specific electrodes. Inductively coupled plasma mass spectrometry (ICP-MS) has been used to determine the concentrations of Na, K, Mg, Ca, SO₄²⁻, Cl⁻, Si, Ag, Al, As, B, Ba, Be, Br, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, P, Pb, Se, Tl, U, V, and Zn using the methods described by Fernández-Turiel et al. (2000a, 2000b).

Isotopic analyses were done at INGEIS Laboratories. ²H in water samples was measured by Coleman et al. (1982) procedure and for the measurement of ¹⁸O was used the methodology described in Panarello and Parica (1984). Isotope ratios were measured with a multicollector McKinney type mass spectrometer, Finnigan MAT Delta S.

The results are expressed like δ, defined as:

$$\delta = 1000 \frac{R_s - R_p}{R_p} \text{‰}$$

δ: isotopic deviation in ‰

S: sample

P: international standard

R: isotopic ratio (²H/¹H, ¹⁸O/¹⁶O).

The standard is Vienna Standard Mean Ocean Water (V-SMOW) (Gonfiantini, 1978).

The analytical errors were ±0.1‰ and ±1.0‰ for δ¹⁸O and δ²H respectively.

RESULTS AND DISCUSSION

Water composition variability

The regional groundwater flow is from WNW to ESE, decreasing the specific conductivity in the same way. In addition to this horizontal trend, results show that the conductivity increases from the higher to the lower topographic levels.

The groundwater pH values varies between 6.00 and 7.86, with a mean value of 6.76 units of pH (Table 1). The major ions characterize the water as sodium bicarbonate type (Fig. 2). The higher SO₄²⁻ and Cl⁻ concentrations are observed in the western sector of the study area. The maximum concentrations are in the Juncal area, decrease towards the city of Pergamino, and increase another

	Groundwater (n=10)			Surface water (n=8)		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
pH	6.00	7.86	6.76	6.44	7.28	6.81
T °C	16.6	19.9	18.5	12.9	17.5	14.2
Cond $\mu\text{S}/\text{cm}$	100	2200	1048	500	1200	857
TDS mg/L	288	1148	547	266	756	443
Na mg/L	172.4	536.8	293.2	124.9	222.6	166.3
K mg/L	10.5	21.6	17.3	16.5	23.9	18.8
Mg mg/L	6.6	18.0	12.2	6.1	23.5	13.5
Ca mg/L	9.5	35.8	20.6	13.7	32.2	19.9
SO ₄ ²⁻ mg/L	11.3	285.2	93.6	43.9	223.6	118.5
Cl ⁻ mg/L	13.6	208.4	68.6	25.1	179.3	86.8
NO ₃ ⁻ mg/L	< 0.1	86.0	43.9	< 0.1	9.0	2.4
HCO ₃ ⁻ mg/L	530.7	975.8	691.7	251.6	359.7	299.1
SIO ₂ mg/L	26.3	30.5	28.6	17.4	23.3	19.8
Ag $\mu\text{g}/\text{L}$	0.01	0.26	0.07	0.01	0.04	0.02
Al $\mu\text{g}/\text{L}$	9	1433	285	1738	3144	2364
As $\mu\text{g}/\text{L}$	21.4	82.0	51.2	11.7	38.1	22.6
B $\mu\text{g}/\text{L}$	350	1642	724	249	322	289
Ba $\mu\text{g}/\text{L}$	27.3	114.2	60.1	31.9	57.8	40.6
Br $\mu\text{g}/\text{L}$	< 50	315	170	< 50	305	143
Cd $\mu\text{g}/\text{L}$	0.03	0.57	0.14	0.05	0.09	0.08
Co $\mu\text{g}/\text{L}$	0.05	0.64	0.14	1.04	2.09	1.54
Cr $\mu\text{g}/\text{L}$	2.96	8.02	5.17	0.75	3.26	1.99
Cu $\mu\text{g}/\text{L}$	2.15	14.88	5.68	3.81	6.49	5.27
Fe $\mu\text{g}/\text{L}$	2	395	67	1401	3248	2450
Hg $\mu\text{g}/\text{L}$	0.00	0.12	0.07	0.00	0.04	0.02
Li $\mu\text{g}/\text{L}$	28.7	57.5	43.2	16.3	28.7	22.8
Mn $\mu\text{g}/\text{L}$	1.1	91.9	12.2	151.5	294.5	213.7
Mo $\mu\text{g}/\text{L}$	6.7	106.2	26.3	4.1	15.0	8.3
Ni $\mu\text{g}/\text{L}$	0.63	1.61	1.09	2.44	3.66	3.06
P $\mu\text{g}/\text{L}$	24	403	142	543	927	773
Pb $\mu\text{g}/\text{L}$	1.17	12.73	5.94	2.32	10.77	5.37
Se $\mu\text{g}/\text{L}$	2.22	16.75	9.43	2.95	16.15	8.43
Tl $\mu\text{g}/\text{L}$	0.00	0.03	0.01	0.04	0.06	0.05
U $\mu\text{g}/\text{L}$	7.31	22.32	12.71	2.93	7.85	4.39
V $\mu\text{g}/\text{L}$	70	290	150	16	76	41
Zn $\mu\text{g}/\text{L}$	10	262	99	12	194	81

Table 1. Minimum, maximum and arithmetic mean of the studied parameters in groundwater and surface water from the Pergamino River watershed (NE Buenos Aires, Argentina).

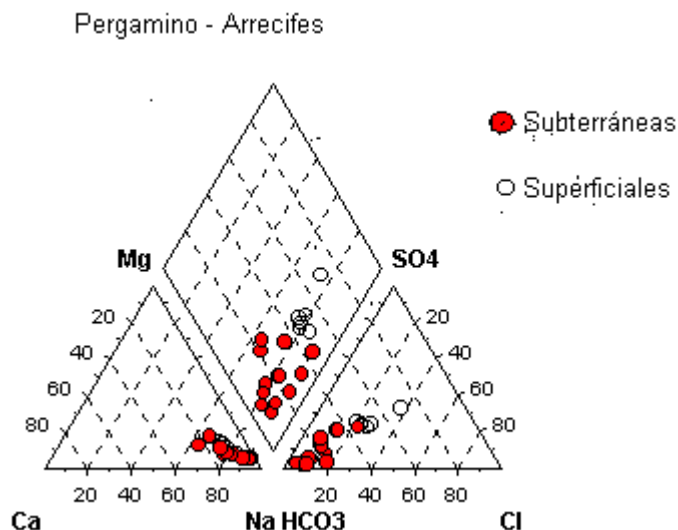


Figure 2. Piper diagram of groundwater and surface water from the Pergamino River watershed (NE Buenos Aires, Argentina).

time in the district of Viña and Todd, at the SE of the area. This fact is associated with the interaction between the local groundwater flow and the lithology (mainly loess with illite as dominant phase) that leachate easily Na-bearing soluble salts. In this water-rock interaction, there is an ion exchange displacing sodium to water and Ca and Mg to the sediment. This process is the origin of the sodium bicarbonate profile of the water. The ion exchange ratio *ier* ($ier = rCl (rNa+rK) / rCl$; where *r* means concentrations expressed as milliequivalent per liter) gives negative values decreasing from west to east (from -2.7 to -12.4) reflecting this sodium enrichment by cation exchange with Ca and Mg (Figure 3).

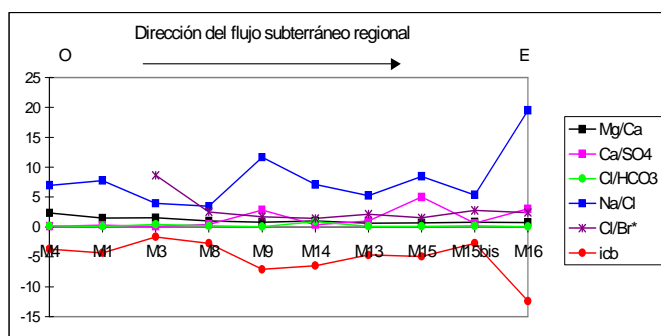


Fig. 3. Groundwater major ion ratios in the Pergamino River watershed (NE Buenos Aires, Argentina). *ier*, ion exchange ratio ($ier = rCl (rNa+rK) / rCl$; where *r* means concentrations expressed as milliequivalent per liter).

The profiles of other ratios of major ions (rMg/rCa , rCa/rSO_4 , rNa/rCl , $rCl/rHCO_3$, and rCl/rBr) corroborates this general trend (Fig. 3). The ratios of rMg/rCa and rCa/rSO_4 show an inverse

behavior. While rMg/rCa decreases from 2.3 to 0.8, the value of rCa/rSO_4 increases from 0.1 to 3.0.

The drainage network drives the water towards the west side of the study area. The low slope of terrain condition a network with flooded areas and swamps. The specific conductivity varies between 500 and 1200 $\mu S/cm$, increasing in the flow river direction. The swamp areas show the maximum values of specific conductivity (for example, 1200 $\mu S/cm$ in sample station M6).

The surface water pH varies from 6.44 to 7.28, being the mean of 6.81 (Table 1). Major ion composition defines a general sodium bicarbonate water type evolving to sodium sulphate-chloride type (Fig. 2). Ca, Mg, SO_4^{2-} , and HCO_3^- concentrations increase in the same way that the general surface flow, while Na+K is practically constant, excepting the sampling stations M7 and M17, where this parameter increases due to the influence of Botija Stream and Los Ingleses Stream, respectively.

The influence of Botija stream affects also the ratios rMg/Ca , rCa/SO_4 and rNa/Cl . They are practically constant in the area (Fig. 4), excepting the sector affected by the influence of the Botija Stream (M7). These changes indicates local variations in the ion exchange processes in the area located upstream the city of Pergamino. On the other hand, the ratio rCl/HCO_3 increases from 0.31 to 4.32 from west to east, with a maximum value of 10.3 at the west of study area. The shallow swamps of this area favors the evaporation and the salt accumulation. The observed Br concentrations have been lower than the detection limit (50 $\mu g/L$) in several sampling stations. The available information points out a slight decrease of the ratio rCl/Br in the flow direction.

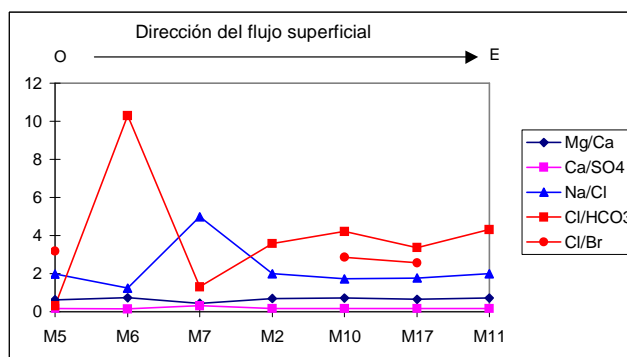


Fig. 4. Surface water major ion ratios in the Pergamino River watershed (NE Buenos Aires, Argentina).

Figure 5 shows the isotopic values obtained from surface and groundwater samples, and the

local meteoric water line (LMWL). This LMWL ($\delta^2\text{H}=8$; $\delta^{18}\text{O}=+14\text{‰}$) was established from a record of more than twenty years of the National Network Collector for Isotopes in Precipitation (RNC) in the Ciudad Universitaria station of Buenos Aires city, which belongs to the Global Network for Isotopes in Precipitation (GNIP) (Panarello et al., 1995, 1998; Dapeña and Panarello, 1999; IAEA/WMO, 2001).

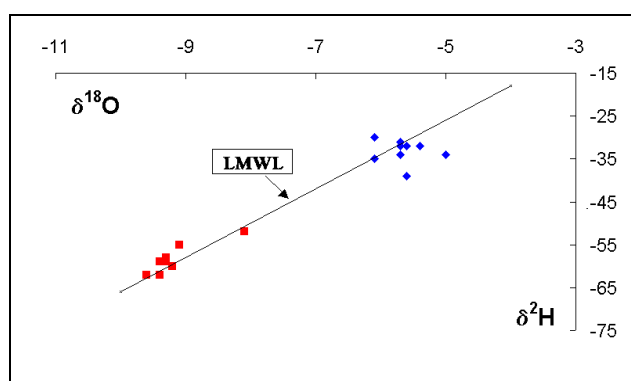


Figure 5. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in groundwater (\blacklozenge) and surface (\blacksquare) water from the Pergamino River watershed (NE Buenos Aires, Argentina). LMWL, local meteoric water line.

The groundwater isotopic composition is relatively constant: $-5,7\text{‰}$ and 33‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Figure 5 and Table 2), close to the average annual precipitation indicating their meteoric origin. Sala et al. (1983) postulated that pampasic lakes were phreatic and the streams were effluents, so the origin of the groundwater is meteoric and the shallow groundwater constitutes the base flow of surface water. In previous works at other localities in the Pampeano aquifer this fact had been demonstrated with isotopic techniques (Panarello et al, 1995; Dapeña et al, 2001). Nevertheless, small fluctuations in the obtained values are probably due to evaporation of local precipitation prior to infiltration. It must be taken into account that recharge waters reflect the mean precipitation with reasonable fidelity (Gat and Gonfiantini, 1981).

The surface water shows a more depleted and also homogeneous isotopic composition, with $-9,2\text{‰}$ and 58‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively (Figure 5 and Table 2). These isotopic values are quite different from the groundwater and are probably due to the combination of three "effects" working together. These effects, known as seasonal, continental and amount, were well studied by Dansgaard (1964). The meteorological analysis of the GNIP data suggests that the large scale synoptic history of the air masses (trajectory, rainout history) is the major factor to control the variability of the isotope data from one rain event to the other and

also the seasonality in the data. On the other hand, factors such as rain intensity (amount) do modify to some extent the isotopic values imposed by synoptic pattern (Gat, 1987). Moreover, it is well established that runoff is the response of an hydrological system to precipitation and involves pre-storm water as well as "direct" precipitation. Isotopically these components can be different and therefore the variation in space and time of the environmental isotopes can provide some insight into runoff mechanisms. So the relative proportions of surface runoff and groundwater discharge can be established. The storm contribution is essentially limited to the rain which had fallen directly on the stream channels (Fritz et al., 1976).

Sampling station	Locality	$\delta^{18}\text{O} \pm 1.0\text{‰}$	$\delta^2\text{H} \pm 0.1\text{‰}$
M1	Well M. Alfonso	-5.6	-32
M3	Well La Rosaura	-5.6	-39
M4	Well Escuela N° 16	-5.7	-34
M8	Well M. Ocampo	-5.7	-31
M9	Well A. Pinzón	-5.7	-34
M13	Well Dulce Pozo	-5.4	-32
M14	Well Rancagua	-5.4	-32
M15	Well Urquiza Anchorena	-5.7	-32
M15b	Well Viña	-6.1	-35
M16	Well Todd	-6.1	-30
M2	Pergamino River	-9.6	-62
M5	Pergamino River swamp	-8.1	-52
M6	Pergamino River	-9.4	-59
M7	Botija Stream	-9.3	-58
M10	Pergamino River (city)	-9.4	-62
M11	Arrecifes River (city)	-9.2	-60
M12	Salto River	-9.3	-59
M17	Pergamino River (bridge)	-9.1	55

Table 2. Water isotopic values of Pergamino River watershed (NE Buenos Aires, Argentina).

In this case, it is known that exist a seasonal pattern in the precipitation from Buenos Aires, Azul, Santa Fe and Corrientes cities and the RNC record shows rains from February to May with $\delta^{18}\text{O}$ varying from -8 to -10‰ reflecting the source of the air masses. But it is also known that the groundwater contributes to the base flow and has an uniform stable isotope composition.

The more depleted values observed in surface water seem reflect a selective influence of the seasonal character of the precipitation as was recorded in isotope rain data from the RNC. ^3H analysis must be carried out in order to confirm this hypothesis. Groundwater responds to the weighted mean annual precipitation, although also is observed

some enrichment by evaporation previous to infiltration.

Water quality

The dominant water type in the region is sodium bicarbonate (Fig. 2). All groundwater samples show this feature. The same trend is observed in the surface waters, although some samples are sodium sulfate-chloride waters (Fig. 2).

The main features related to the water quality have been analyzed by comparison with the Argentinean legal rules (Código Alimentario Argentino of 1994 and Law 24.051 de Residuos Peligrosos of 1993) (Tables 3 to 5). The pH values are lower than 6.5 units (lower threshold of human drinking water pH interval) in 20 and 10% of groundwater and surface water samples, respectively. Nitrate concentration exceeds the human drinking water reference threshold (45 mg/L) in 50% of the sampled wells. The mean nitrate concentration is 43.9 and 2.4 mg/L for groundwater and surface water (Table 3). The variability of this parameter is unrelated to the regional water flow, being associated with point pollution sources.

	Human drinking water reference level	Groundwater (% samples)	Surface water (% samples)
pH	6.5 - 8.5	20	10
TDS mg/L	1500	0	0
Alkalinity	400	n.d.	n.d.
Hardness	400	n.d.	n.d.
SO ₄ ²⁻ mg/L	400	0	0
Cl mg/L	350	0	0
NO ₃ ⁻ mg/L	45	50	0
NO ₂ ⁻ mg/L	0.1	n.d.	n.d.
NH ₃ mg/L	0.2	n.d.	n.d.
F mg/L	0.7 - 1.2	n.d.	n.d.
CN ⁻ mg/L	0.1	n.d.	n.d.
Ag µg/L	50	0	0
Al µg/L	200	10	100
As µg/L	50	40	0
B µg/L (*)	1000	20	0
Ba µg/L (*)	1000	0	0
Be µg/L (*)	0.039	n.d.	n.d.
Cd µg/L	100	0	0
Cr µg/L	50	0	0
Cu µg/L	1000	0	0
Fe µg/L	300	10	100
Hg µg/L	1	0	0
Mn µg/L	100	0	100
Ni µg/L (*)	25	0	0
Pb µg/L	50	0	0
Tl µg/L (*)	18	0	0
U µg/L (*)	100	0	0
Zn µg/L	5000	0	0

Table 3. Percentage of samples exceeding the reference levels for human drinking water in the Pergamino River watershed (NE Buenos Aires, Argentina). Reference levels from Codigo Alimentario Argentino of 1994, with the exception of elements indicated as (*) that are from the Argentinean Law 21.054. n.d., parameter not determined.

	Irrigation reference level	Groundwater (% samples)	Surface water (% samples)
Al µg/L	5000	0	0
As µg/L	100	0	0
B µg/L	500	90	0
Be µg/L	100	n.d.	n.d.
Cd µg/L	10	0	0
Co µg/L	50	0	0
Cr µg/L	100	0	0
Cu µg/L	200	0	0
F µg/L	1000	n.d.	n.d.
Fe µg/L	5000	0	0
Li µg/L	2500	0	0
Mn µg/L	200	0	50
Mo µg/L	10	90	37
Ni µg/L	200	0	0
Pb µg/L	200	0	0
Se µg/L	20	0	0
U µg/L	10	60	0
V µg/L	100	80	0
Zn µg/L	2000	0	0

Table 4. Percentage of samples exceeding the reference levels for irrigation in the Pergamino River watershed (NE Buenos Aires, Argentina). Reference levels from Argentinean Law 21.054. n.d., parameter not determined.

	Cattle drinking water reference level	Groundwater (% samples)	Surface water (% samples)
Al µg/L	5000	0	0
As µg/L	500	0	0
B µg/L	5000	0	0
Be µg/L	100	n.d.	n.d.
Cd µg/L	20	0	0
Co µg/L	1000	0	0
Cr µg/L	1000	0	0
Cu µg/L	1000	0	0
F µg/L	1000	n.d.	n.d.
Hg µg/L	3	0	0
Mo µg/L	500	0	0
Ni µg/L	1000	0	0
Pb µg/L	100	0	0
Se µg/L	50	0	0
U µg/L	200	0	0
V µg/L	100	80	0
Zn µg/L	50	60	50

Table 5. Percentage of samples exceeding the reference levels for cattle drinking water in the Pergamino River watershed (NE Buenos Aires, Argentina). Reference levels from Argentinean Law 21.054. n.d., parameter not determined.

In relation to the trace elements, those elements that exceed some of the respective reference thresholds are Al, As, B, Fe, and Mn for human drinking water, B, Mo, U, V for irrigation, and V and Zn for cattle drinking water.

The observed aluminum concentrations indicate that the groundwater and surface water are adequate for irrigation and cattle consumption. However, 10% of groundwater samples and all surface water samples exceed the human drinking water threshold of 200 µg/L. The aluminum concentration increases in the direction of regional water flow, decreasing by mixing with the water of Botija Stream and Los Ingleses Stream.

The arsenic concentration of forty percent of groundwater samples exceeds the human drinking water threshold (50 µg/L), being the mean concentrations of 51.2 and 22.6 µg/l of As for groundwater and surface water samples, respectively. However, both water types can be used for irrigation and cattle consumption. These values are similar to other observed in the region (Galindo et al., 1999). The volcanic ashes included in the sedimentary sequence could be the source of this trace element. Other possible source is the anthropogenic input by means of weed-killers (arsenite) and insecticides (arsenate), both commonly used in the area.

The boron concentrations are higher in groundwater than in surface water, with mean values of 724 and 289 µg/L of B, respectively. In fact, 20% of sampled wells present concentrations exceeding the regulated threshold for human drinking water (1000 µg/L), while 90% are higher than the irrigation threshold (500 µg/L). There are not potentially risk for cattle consumption (Table 5). The observed boron concentrations are associated with, as in the case of As, pyroclastic levels included in the sedimentary sequence.

Ten percent of groundwater and all surface water sampling stations show iron concentrations inadequate for human drinking water purposes without treatment. A similar feature is presented by manganese, but only in the surface water. The presence of humic substances and CO₂ in the water favor the mobilization of such elements. In addition, also must be considered the anthropogenic contribution of point pollution sources. The observed concentrations are adequate for cattle consumption.

The local pH-Eh conditions facilitate the Mo and U mobilization, presumably from the before mentioned pyroclastic levels. In relation with the considered regulations, the groundwater has a potential risk for irrigation, exceeding the threshold of 10 µg/l of Mo and U in 90% and 60% of wells, respectively. The concentrations determined in 37% of the surface water sampling stations also are higher than this value for Mo.

The concentrations of vanadium in groundwater are inadequate for irrigation and cattle consumption in 80% of wells. The mean concentration for groundwater is of 150 µg/L of V and the threshold for these uses is 100 µg/L of V. The origin of vanadium is associated with the weathering of igneous rocks and its by-products.

Finally, the concentration of zinc is higher than the threshold regulated for cattle consumption

in 60% of the sampled wells and in 50% of the surface water sampling stations.

CONCLUSIONS

Groundwater and surface water from the Pergamino watershed are of sodium bicarbonate type, evolving to sodium sulfate-chloride type in the case of surface water. Water composition variability evidences the regional water flow from WNW-ESE and the local recharges and discharges, being influenced mainly for the alternating humid and dry climate periods (precipitation and evapotranspiration), and for rock-water ion exchange processes. In addition to these natural processes, there are point pollution sources (septic wells and other domestic effluents) that induce the increase of nitrate concentration and, possibly, Fe and Mn concentrations.

In relation to water quality, pH, NO₃⁻, Al, As, B, Fe, and Mn exceed the respective Argentinean reference thresholds in different sampling stations for human drinking water, B, Mo, U, V for irrigation, and V and Zn for cattle drinking water. An improvement of waste water management will affect practically only the nitrate concentration on groundwater and Fe and Mn concentrations in surface water, due to the levels of the other potentially dangerous parameters are consequence of natural processes. Thus, the water quality situation is spatially heterogeneous and every case must be considered separately. More research is necessary to determine the best supply source at this local level and if it is feasible (technically and economically) some specific treatment for a determined use.

ACKNOWLEDGEMENTS

The authors wish to thank the technical support of the personnel from the INGEIS Laboratories and the Scientific-Technical Services of the University of Barcelona. This work has been partially funded through the Project PEI 0112/98 from CONICET and Project T657 from University of Buenos Aires.

REFERENCES

Coleman, M.L., Sheperd, T.J., Durham, J.J., Rouse, J.E. and Moore, F.R., 1982. A rapid and precise technique for reduction of water with zinc for hydrogen isotope analysis. *Analytical Chemistry*: 54: 993-995.

- Dansgaard, W., 1964. Stable Isotopes in precipitation. *Tellus*, 16: 436-468.
- Dapeña, C., Panarello, H.O., 1999. Development of the National Network for Isotopes in Precipitation of Argentina. II South American Symposium on Isotope Geology, 503-508.
- Dapeña, C., Miretzky, P., Panarello, H. O., Fernández Cirelli, A., 2001. Environmental stable isotope of the "Sistema de Las Encadenadas de Chascomús", Buenos Aires, Argentina. III South American Symposium on Isotope Geology, Sociedad Geológica de Chile, Santiago de Chile. Extended Abstracts Volume, 375-378.
- Fernández-Turiel J.L., Llorens J.F., López-Vera F., Gómez-Artola C., Morell I., Gimeno D., 2000a. Strategy for water analysis using ICP-MS. *Fresenius' Journal of Analytical Chemistry*, 368-6: 601-606.
- Fernández-Turiel J.L., Llorens J.F., Roig A., Carnicero M., Valero F., 2000b. Monitoring of drinking water treatment plants using ICP-MS. *Toxicological and Environmental Chemistry*, 74: 87-103.
- Fritz, P., Cherry, J.A., Weyer, K.U., Sklash, M., 1976. Storm runoff analyses using environmental isotopes and major ions. Proceedings of the symposium of Interpretation of environmental isotope and hydrochemical data in groundwater hydrology. International Atomic Energy Agency, Vienna, 111-130.
- Galindo G., Herrero M.A., Flores M., Fernández-Turiel J.L., 1999. Correlación de metales trazas en aguas subterráneas someras de la Cuenca del Río Salado, Provincia de Buenos Aires, Argentina. In: A. Tineo (Ed.), *Hidrología Subterránea*, II Congreso Argentino de Hidrogeología y IV Seminario Hispano Argentino sobre temas actuales de la Hidrología Subterránea. Serie Correlación Geológica n° 13, Instituto de Correlación Geológica – CONICET, Fac. Cs. Nat. e Inst. Miguel Lillo de la Univ. Nac. de Tucumán, pp. 251-261.
- Gat, J., Gonfiantini, R., 1981. Stable Isotope Hydrology. Deuterium and Oxygen-18 in the water cycle. Technical Reports Series N° 210. International Atomic Energy Agency. Vienna. 337 p.
- Gat, J., 1987. Variability (in time) of the isotopic composition of precipitation: consequences regarding the isotopic composition of hydrologic systems. Proceedings of the Symposium of isotope techniques in water resources development. International Atomic Energy Agency, Vienna, 551-563.
- IAEA/WMO, 2002. Global Network for Isotopes in Precipitation. The GNIP Database. <http://isohis.iaea.org>.
- Losinno, B., Heredia, O., Sainato, C., Giuffré, L., Galindo, G., 2002. Impacto potencial del riego con agua subterránea sobre los suelos en la cuenca del arroyo Pergamino, Pcia. de Bs. As., Argentina. *Ecología Austral*, in press.
- Panarello, H.O., Parica, C.A., 1984. Isótopos del oxígeno en hidrogeología e hidrología. Primeros valores en aguas de lluvia de Buenos Aires. Asociación Geológica Argentina, Revista XXXIX (1-2): 3-11.
- Panarello, H.O., Dapeña, C., Auge, M.P., 1995. Mecanismos de salinización del agua subterránea de la zona de La Plata, Buenos Aires, Argentina: su interpretación por medio de los isótopos ambientales. International Atomic Energy Agency Technical Document 835: 13-27.
- Panarello, H.O., Araguas-Araguas, L., Gerardo-Abaya, J., Gibert, E., 1998. The role of the Global Network for Isotopes in precipitation (GNIP) in hydrological and hydro-climatic studies. Key note of the International Symposium on Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere. *Isotope Techniques in the Study of Environmental Change*: 79-91.
- Sainato, C.M., Galindo, G., Pomposiello, M.C. and Malleville, H., 1997. Hidrogeología de la cuenca del arroyo Pergamino. 19° Reunión Científica de la Asociación Argentina de Geofísicos y Geodestas. San Juan. Argentina.
- Sainato, C., Losinno, B., Landini, A., Pomposiello, M.C., Malleville, H. 2001. Estudio de los acuíferos de la zona de Arrecifes (Pcia. de Bs. As., Argentina) mediante sondeos eléctricos verticales. 7th International Congress of the Brazilian Geophysical Society. Salvador. Brasil.
- Sainato, C., Pomposiello, M.C., Landini, A., Galindo, G., Malleville, H., 2002. The hydrogeological sections of the Pergamino basin (Bs. As. Province, Argentina): Audiomagnetotelluric and geochemical results. *Revista Brasileira de Geofísica*, 18: in press.
- Sala, J., Gonzalez, N., Kruse, E., 1983. Generalización Hidrológica de la Provincia de Buenos Aires. Coloquio Internacional de Grandes Llanuras. Olavarría. Provincia de Buenos Aires. UNESCO. Vol. III: 975-1008.
- Santa Cruz, J., Silva Busso, A., 1995. Disponibilidad del agua subterránea para riego complementario en las Provincias de Bs. As., Entre Ríos, Córdoba y Santa Fe. Programa de Servicios

Agrícolas provinciales. Secretaría de Agricultura, Ganadería y Pesca. Argentina. 55 pp.

